

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number
WO 00/77070 A2

- (51) International Patent Classification⁷: C08G 63/60 (74) Agent: KIRK, Martin; UCB, S.A., Intellectual Property Dept., Allée de la Recherche 60, B-1070 Bruxelles (BE).
- (21) International Application Number: PCT/EP00/05191
- (22) International Filing Date: 6 June 2000 (06.06.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/138,285 9 June 1999 (09.06.1999) US
- (71) Applicant (for all designated States except US): UCB, S.A. [BE/BE]; Allée de la Recherche 60, B-1070 Bruxelles (BE).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): VERSCHUEREN, Kris [BE/BE]; E. De Blutslaan 38, B-1702 Groot-Bijgaarden (BE). VANOVERVELT, Jean-Claude [BE/BE]; Rue Albert 26, B-7548 Warchin (BE). DE MICHELI, Philippe [BE/BE]; Rue de Marchienne 146, B-6110 Montigny-Le-Tilleul (BE).
- Published:
— Without international search report and to be republished upon receipt of that report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 00/77070 A2

(54) Title: MODIFIED HYPERBRANCHED POLYESTER POLYMERS, PROCESSES FOR PREPARING THEM AND USES OF THEM

(57) Abstract: The hyperbranched polymers (polyester polyol) can be modified and that modified hyperbranched polymers have improved characteristics. The high functionality of hyperbranched polymers allows for chemical and/or physical modifications to achieve certain mechanical, chemical or physical properties. Such modified hyperbranched polyester polyols can be tailored through consecutive or mixed end-capping to obtain either very specific or mixed properties. It is possible to use these modified hyperbranched polyester polyols in new industrial applications, such as inks.

Best Available Copy

MODIFIED HYPERBRANCHED POLYESTER POLYMERS, PROCESSES FOR PREPARING THEM AND USES OF THEM

BACKGROUND OF THE INVENTION

5

Field of the invention

The present invention relates to modified hyperbranched polyester polymers, processes for preparation of these modified hyperbranched polymers and the uses of such polymers.

Description of related art

10 Hyperbranched polymers can be described as consisting of a core of a polyfunctional molecule, an intermediate, tree structured layer formed by successive branching reactions, and a shell constituted by extending branches carrying functionalities.

In the European patent 0 630 389, particular hyperbranched polymers, named dendritic macromolecule by the patentee, are described and also named polyester polyols. These
15 macromolecules are composed of a central initiator molecule having one or more hydroxyl groups, which groups under formation of an initial tree structure are bonded to carboxyl groups of a monomeric chain extender. The dendritic macromolecule can be further extended by a reaction with a chain stopper. In the European patent 0 630 389, the core materials used are polyols, such as trimethylolpropane, ditrimethylolpropane and pentaerythritol. The
20 exemplified monomeric chain extender is dimethylolpropionic acid. The exemplified chain stopper are lauric acid, soybean fatty acid, capric acid, caprylic acid and tall oil fatty acid.

In fact, typical macromolecule products bearing hydroxyl groups at its peripheral surface are obtained, by acid catalyzed esterification between pentaerythritol (PETA), the core material, considered to be a chain stopper, and dimethylolpropionic acid (DMPA) which make the shell
25 of the structure. From one mole of PETA and 12 moles of DMPA, a tree-like polydric polyester with 16 external hydroxyl groups is obtained. Such a product is described as a hyperbranched structure from the second generation (two successive esterifications). The homologue product pertaining to the third generation (approximately molecular weight of 3600 g/mole) bears 32 primary hydroxyl functions.

30

BRIEF SUMMARY OF THE INVENTION

It has been discovered that the hyperbranched polyester polymers can be modified and that modified hyperbranched polymers have improved characteristics. The high functionality of hyperbranched polymers allows for chemical and/or physical modifications to achieve certain
35 mechanical, chemical or physical properties. Such polyester polymers can be tailored through consecutive or mixed end-capping to obtain either very specific or mixed properties.

Consequently, it is possible to use these modified hyperbranched polymers in new industrial applications.

The hydroxyl functions of the hyperbranched polymers are modified via chemical reaction, such as esterification reaction.

Reacting with a chemical compound modifies at least a part of the hydroxyl functions of the hyperbranched polymers, in some cases all of the hydroxyl functions.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hyperbranched polyester polyol composed of a central initiator molecule or initiator polymer having two or more hydroxyl groups, which groups under formation of an initial tree structure are bonded to carboxyl groups of a monomeric chain extender holding the hydroxyl groups and the carboxyl groups, which tree structure optionally is extended and further branched from the initiator molecule or initiator polymer by an addition of further molecules of a monomeric chain extender by means of bonding between the hydroxyl groups and the carboxyl groups thereof, wherein the hyperbranched polyester polyol is modified via esterification reaction on at least one hydroxyl group by at least one carboxylic acid and by at least another acid chosen among acrylic acid, methacrylic acid and oligomers thereof.

15

Unmodified hyperbranched polyester polyol are known per se, such as, but without limitation, in European patent application 0 630 389, or international patent application WO 96/07688, or international patent application WO 93/17060.

20

By oligomers of acrylic acid and methacrylic acid, we understand products resulting from the consecutive Michael addition of a carboxylic group belonging to an (meth)acrylate compound onto a double bond belonging to another (meth)acrylate compound. Examples of oligomers are dimers and trimers of acrylic acid, such as, preferably, dimer of acrylic acid : β -carboxyethyl acrylate.

25

The definition of a carboxylic acid does not include acrylic acid, methacrylic acid and oligomers thereof, in the present invention.

The modified hyperbranched polyester polyols can have different degrees of modification.

Consequently, they contain a variable percentage of free hydroxyl group, a variable percentage of hydroxyl groups which have been acrylated with acrylic acid, methacrylic acid or oligomers thereof, and a variable percentage of hydroxyl groups which have been esterified with carboxylic acid. These percentages have an effect on properties of the obtained product, such as reactivity, rheology.

30

The percentage of free hydroxyl group comprises from 0 to about 99 % based on the initial hydroxyl content of the polyester polyol. The percentage of free hydroxyl group comprises from 0 to about 50 %, and most preferably from 0 to about 35 %. The best results have been obtained from about 0.5 to about 15 % (% based on equivalent).

35

The percentage of hydroxyl groups which have been acrylated with acrylic acid, methacrylic acid or oligomers thereof, comprises from about 20 to about 99 % based on the initial hydroxyl

content. The percentage is comprises preferably from about 30 to about 90 %, and most preferably from about 40 to about 85 %. The best results have been obtained from about 45 to about 75 % (% based on equivalent).

The percentage of hydroxyl groups that have been esterified with carboxylic acid group(s) comprises from about 5 to about 80 % based on the initial hydroxyl content. The percentage comprises preferably from about 10 to about 70 %, and most preferably from about 15 to about 60 %. The best results have been obtained from about 20 to about 50 % (% based on equivalent).

The present invention also relates to a process for preparation of a modified hyperbranched polyester polymer as disclosed above. In view to obtain the appropriate properties as disclosed above, the process can be performed in one or two reaction steps.

The process is preferably characterised in that it comprises a first esterification step in which a hyperbranched polyester polyol is reacted with a carboxylic acid and a second acrylation step in which the compound obtained in the first step is reacted with acrylic acid, methacrylic acid or oligomers thereof.

The process for the preparation of a modified hyperbranched polyester polyol can also be characterised in that it comprises a first acrylation step in which a polyester polyol is reacted with acrylic acid, methacrylic acid or oligomers thereof, and a second esterification step in which the compound obtained in the first step is reacted with a carboxylic acid.

The process for the preparation of a modified hyperbranched polyester polyol can also be characterised in that the polyester polyol is reacted with a carboxylic acid and with acrylic acid, methacrylic acid or oligomers thereof, in one step.

The esterification step comprises a reaction with a carboxylic acid. By carboxylic acid, we understand an acid linear or branched, saturated or unsaturated, preferably it is monocarboxylic acid having at least a molecular weight of 60, and most preferably of 88.

Examples of saturated carboxylic acid are acetic acid, propionic acid, butyric acid, valeric acid, isobutyric acid, trimethylacetic acid, caproic acid, caprylic acid, heptanoic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and dimeric and trimeric acids derived from unsaturated fatty acids (such as the product range sold under the trademark PRIPOL by the company UNIQUEMA). Good results have been obtained with propionic acid, lauric acid and stearic acid. The best results have been obtained with lauric acid.

Examples of unsaturated carboxylic acids suitable for this purpose are oleic acid, ricinic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, soybean fatty acid, linseed fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid, safflower fatty acid.

The esterification step is preferably performed in the presence of a solvent such as an apolar organic solvent like heptane, cyclohexane, toluene, benzene, xylene or mixtures thereof, preferably toluene.

The esterification step is preferably performed in the presence of a catalyst, such as p-toluenesulfonic acid, methanesulfonic acid, trifluoromethane sulfonic acid, trifluoroacetic acid, sulfuric or phosphoric acid, naphthalene sulfonic acid, Lewis acids such as BF_3 , AlCl_3 , SnCl_4 , titanates such as tetrabutyl titanates, organotin compounds, preferably

5 p-toluenesulfonic acid.

The esterification step preferably takes place at a temperature from about 50 to about 280 °C, preferably from about 100 to about 250 °C depending upon the selected solvent, the reaction conditions and upon pressure.

It is also possible to incorporate an alkyl chain by using an alkanoyl halide, such as a

10 compound of general formula R-CO-X , in which X represents a halogen such as Cl, Br, and R represents an alkyl group, preferably having from 4 to 20 carbon atoms. Suitable examples of alkanoyl halides are lauroyl chloride and hexanoyl chloride.

The acrylation step comprises a reaction with acrylic acid, methacrylic acid or oligomers thereof.

15 The acrylation step is performed in the presence of a solvent such as an apolar organic solvent like heptane, cyclohexane, toluene, benzene, xylene or mixtures thereof, and preferably toluene.

The acrylation step is preferably performed in the presence of a catalyst, such as p-toluenesulfonic acid, methanesulfonic acid, trifluoromethane sulfonic acid, trifluoroacetic

20 acid, sulfuric or phosphoric acid, naphthalene sulfonic acid, Lewis acids such as BF_3 , AlCl_3 , SnCl_4 , titanates such as tetrabutyl titanates, organotin compounds, preferably the same catalyst as used in the esterification step and more preferably p-toluenesulfonic acid.

The acrylation step is preferably performed in the presence of a radical polymerisation inhibitor, such as inhibitor described in U.K. patent 2 025 996, and, in particular, methyl

25 ether hydroquinone (MeHQ), or hydroquinone, phenothiazine, di-t-butyl hydroquinone, or a mixture of them, and preferably MeHQ.

The acrylation step preferably takes place at a temperature from about 50 to about 200 °C and preferably from about 80 to about 150 °C, depending upon the selected solvent, the reaction conditions and upon pressure.

30 Another process for preparing a modified hyperbranched polyester polymer comprises a conversion step of a hyperbranched polyester polyol to an acrylated or methacrylated hyperbranched polyester polyol by reacting a hyperbranched polyester polyol with acrylic anhydride or methacrylic anhydride.

Another process for preparing a modified hyperbranched polyester polymer comprises the

35 reaction step of a hyperbranched polyacid with glycidyl acrylate or glycidyl methacrylate in the melt.

The reaction preferably takes place at the temperature from about 80 to about 160 °C.

The invention also relates to the use of a modified hyperbranched polyester polyol as component in applications such as binders for radiation curing systems such as systems cured with ultra-violet (UV) and infra-red (IR) or electron-beam (EB). The modified hyperbranched polyester polyols of the invention are resins and, as such, can be used to prepare radiation curable inks by addition of pigments and additives. It is particularly useful for flexographic inks, letterpress inks, lithographic inks, gravure inks and jet inks. It is in general used to prepare pigmented formulations for applications that require good wetting of these pigments, excellent flow properties and low yield values (such as described in The Printing Ink Manual, 5th edition, R.H. Leach and R.J. Pierce, Ed. Blueprint (London), 1993).

The modified hyperbranched polyesters polyols of the invention can be formulated with pigments and additives to form an ink. These inks can be used in flexography, gravure, lithography and screen printing, good results have been obtained with flexography. The modified hyperbranched polyester polyols of the invention have an adequate viscosity for grinding, good pigment wetting characteristics, good flow properties after pigment incorporation, appropriate viscosity, low odour after curing. The inks comprising the modified hyperbranched polyester polyols of the invention have an adequate viscosity, a good adhesion, a good UV reactivity, a good EB reactivity, low yield values and good compatibility with acrylated products (monomers, oligomers).

The following examples are present to give those skilled in the art a better understanding of the claimed invention. The examples are in no way intended to limit the invention.

EXAMPLES

Example 1

In a double-wall glass reactor with a capacity of 5 l and fitted with an agitator, a thermometer, a nitrogen inlet tube, a connection to vacuum and an azeotropic distillation column, 1000 g of polyester polyol (0.57 mol., 1 equivalent OH) sold by Perstorp under the trademark Boltorn H-20, 351 g (1.82 mol., 0.2 equivalent (eq.)) lauric acid, 1.5 % p-toluenesulfonic acid (PTSA), are dissolved in toluene (1174 g, i.e. 40 weight-% on total).

This mixture is heated to reflux (about 110 °C) and stirred until all the water is distilled over (= 33 ml).

Then, 568 g (8.19 mol., 0.9 eq.) acrylic acid, and 1000 ppm methyl ether hydroquinone (MeHQ) are added and stirring is continued at 110 °C. Oxygen is injected to prevent gelling. When all the water is distilled over (= 131 ml) the mixture is cooled to 60°C and toluene (587 g) added to reach an end concentration of 50 % toluene.

This mixture is washed four times with water (20 weight % on total) containing 20 % NaCl, dried via azeotropic distillation to remove all the water and finally filtered.

The toluene was distilled and stripped under high vacuum (30 mmHg) to remove all traces of toluene.

Properties of the obtained resin are given in Table 1.

Viscosity (25 °C, mPa.s, Höppler) of the resin was measured according to the method described in DIN 53015.

5 Reactivity (m/min) of the resin was the speed of the belt at which a film is dry after passing one time under an UV (ultra-violet) lamp (power 80 W/cm).

Examples 2-10

The procedure according to example 1 was repeated with the difference of charges of lauric acid and acrylic acid. Charges of lauric acid and acrylic acid are given in table 1.

10 Properties of the obtained resins are given in Table 1.

Example 11

The procedure according to example 1 was repeated with a charge of 1000g (0.57 mol, 1 equivalent OH) of polyester polyol sold by Perstorp under the trademark Boltorn H-20, 328 g (4.55 mol, 0.5 eq.) acrylic acid and 337 g (4.55 mol, 0.5 eq.) propionic acid.

15 The obtained resin has a theoretical composition acrylic acid/propionic acid : 50/50 % (based on equivalent).

Example 12

20 The procedure according to example 1 was repeated with a charge of 1000g (0.57 mol, 1 equivalent OH) polyester polyol sold by Perstorp under the trademark Boltorn H-20, 328 g (4.55 mol, 0.5 eq.) acrylic acid and 1299 g (4.55 mol, 0.5 eq.) stearic acid.

The obtained resin has a theoretical composition acrylic acid/stearic acid : 50/50 % (based on equivalent).

25 Examples 13-22

The viscosity of the resins obtained according to examples 1 to 10 was adjusted with OTA 480 (trifunctional oligoacrylate available from UCB, S.A.) to match the viscosity of EB 450 (fatty acid modified hexafunctional polyester acrylate available under the trademark EBECRYL from UCB, S.A.), equal to 7500 mPa.s.

30 The pigment wetting was quantified using flow-measurements on a glass plate at a 45° angle (distance in cm after 1 minute). Results are given in table 1 (flow Black paste in cm).

35 Viscosity (25 °C, mPa.s, Brookfield) of the resins with adjusted viscosity was measured according to the method described in ASTM D 2849. The ink was formulated as follows: resin + OTA 480 :100, carbon black: 20 and Darocure 1173 : 6. The product sold under the trademark Darocure 1173 is available from Ciba. The product sold under the trademark OTA 480 is available from UCB, S.A.. The product carbon black, sold under the trademark Spezialschwarz 250 is available from Degussa.

Table 1

Examples	Resin			resin with adjusted viscosity			ink	
	Theoretical Resin Composition AA/Lauric acid/free OH % (based on equivalent)	Viscosity (25°C, mPa.s) Höppler	Reactivity + OTA (m/Min)	+ OTA %	Viscosity (25°C, mPa.s) (m/min)	Reactivity (m/min) Brookfield	Reactivity Ink (m/min)	flow (cm) Black Paste + 10 % OTA
EB 450		7500	30	0	7500	30	20	3.8
1	80/20	31516	20	20	7016		25	5.8
2	50/20/30	16211 (60°C)	20	42	7500	15	20	10
3	50/50	8000	< 5	0	8000	< 5	10	6
4	70/20/10	25070	30	18	8000	20	20	4.9 (∞)
				16	9500			
5	70/30	14560	15	11.5	8100	15	30	5.4
6	60/40	9660	10	5.7	7750	15	15	3.1
7	50/40/10	7630	10	0	7630	5	20	5.9
8	50/30/20	20240	20	15	8000	10	10	6.6
9	60/20/20	34340	10	21	8200	15	40	3.1
10	60/30/10	16900	10	12	8600	10	10	6.2 (20 % carbon black)

In table 1, AA represents acrylic acid; free OH represents the theoretical percentage (based on equivalent) of non reacted hydroxyl groups; OTA % (in the paragraphs "resin with adjusted viscosity" and "ink") represents the percentage of OTA 480 based on weight.

The resins obtained according to examples 1 to 10 and the resin EB 450 were mixed with 6% (on weight) Darocure 1173.

The degree of curing under UV of these blends was measured by attenuated total reflectance FTIR (infra red method). The % reacted acrylic unsaturation (% RAU) for a few, clear varnish, formulation was calculated. Results are given in table 2.

The change in acrylic absorption at 1410 cm^{-1} (in-plane bending) was recorded in multiple internal reflectance (MIR). Variations in film thickness were compensated by normalising the acrylate absorption to a band which remains constant during the curing. An asymmetric CH-stretching vibration at 2924 cm^{-1} was chosen as internal standard and the relative absorbance Ar is defined as

$$Ar = \frac{A(1410)}{A(2924)}$$

where $A(1410)$ is the absorbance at 1410 cm^{-1} , and $A(2924)$ is the absorbance at 2924 cm^{-1} . The relative absorbance is used to calculate the percent reacted acrylate unsaturation (% RAU) according to the following equation

$$\%RAU = \frac{A_{ro} - A_{rt}}{A_{ro}} \times 100$$

Where A_{ro} is the relative absorbance of the uncured film, and A_{rt} is the relative absorbance of the cured film.

Table 2

Resin	Curing Conditions m/min	% RAU
8	20*	95
8	3 x 20	>99
9	10*	98
9	3 x 10	>99
EB450	25*	62
EB450	3 x 25	72

* tack-free

These results indicate a very high conversion.

These results indicate that, in comparison with a conventional fatty acid modified polyester, the use of modified hyperbranched polyester polyols allows to reach a very low level of unreacted unsaturation.

Examples 23-29

To the resin obtained according to examples 2, 4, 5 and 10 was added a yellow pigment sold under the trademark Irgalite yellow BAW 80/20 by Ciba. An ink was obtained.

The viscosity of the obtained ink was adjusted with OTA 480 to match the viscosity of EB450, quantities of OTA 480 added are given in table 3.

Flow was measured. The results are given in table 3.

Table 3

Resin		Reference EB 450	2	4	Examples		
OTA	%	0	42	0	25	0	0
flow	cm	3.6	2.8	3.6	2.5	3.3	3.5

Example 30

The resin obtained according to example 7 was added to EB 450 in an amount defined in table 4 (% based on weight).

A yellow pigment sold under the trademark Irgalite yellow BAW 80/20 was added in an amount of 20 % (weight). OTA 480 was added in an amount of 16 % on weight.

An ink was obtained. Flow of the ink was measured. Results are given in table 4.

Table 4

Resin example	Flow (cm)			
	% added resin to EB 450			
	0	5	10	20
EB 450	4			
Example 7	-	5	5.4	5.7

In order to improve the flow and to lower yield values in final formulated systems, the materials were tried in combination with EB 450 to see the influence on rheology (cone plate viscometer)

Example 31

All resins (obtained according to examples 4, 5, 7, 8, 9 and 11) were tested in a pigment dispersion, based on three roller mill formulations and diluted in a letdown vehicle (the same type as used in the ink industry).

A pigment base was formed as following :

- resin 55 – 65 %

obtained in examples 1 - 10

- DPGDA 0 – 15 % (depending on the viscosity of the resin) DPGDA represents
dipropyleneglycol diacrylate, a product sold by UCB, S.A.

5 - Dispersant 0 or 4 %

dispersant sold under the trademark IRR 434 from UCB, S.A.

- Pigment 35 %

pigment sold under the trademark Irgalite GLO: phtalo blue by CIBA.

An ink was formed as following :

10 - pigment base 40 %

- EB 40 51.5 %

acrylated tetrafunctional oligomer available from UCB, S.A.

- Photoinitiator 8 %

product available from CIBA under the name Speedcure

15 - Siliconised levelling agent 0.5 %

product PA 57 available from Dow Corning.

The inks were printed and compared against a reference ink (a commercial ink available from
SUN CHEMICAL under the trademark 50 HF 07).

The following parameters were evaluated :

20 - The optical aspect of the printed film, such as gloss, transparency, colour intensity and
shade purity was defined as appearance and measured by visual inspection in comparison
with the reference (1 is bad, 5 is best)

- Rheology of the inks at very low shear ($0.1 - 1 \text{ s}^{-1}$ shear rate) (Casson Model described in
Emulsions and Emulsion Technology, part III, ed. by Kenneth J. Lissant, Marcel Dekker,
25 Inc, 1984, pp. 66).

A good ink should give a glossy, transparent, pure and intense print, no haze and have a low
viscosity at low shear and a flat curve.

The following results were obtained:

Rheology: the viscosity at very low (0.1 s^{-1}) and high (1 s^{-1}) shear rate were compared.

30 Results are given in table 5.

Table 5

Resin	D (s ⁻¹)		appearance
	0.1 tau (Pa)	1 tau	
Reference	3.89	7.11	3
Example 7	0.92	3.25	2
Example 9	0.55	2.32	3
Example 8	0.65	2.38	2
Example 11	0.67	2.42	4
Example 4	0.63	2.57	5
Example 5	0.56	2.35	4

Reference represents a commercial resin ink sold by SUN CHEMICAL under the trademark 50 HF07.

Some trials were also performed using 20 % pigment sold under the trademark Novoperm Gelb P-HG available from Clariant.

All the study was done on a cone plate viscometer and Yield value (tau (Pa)) was determined using the Casson Model.

All the measurements have been done at a low shear rate between 0 and 5 s⁻¹ with the HAAKE rheometer (system CV 100 : PK 20-4°). The flow curves tau (shear stress in Pa) as a function of D (shear rate in s⁻¹) has been measured and is described by means of a mathematical model, the Casson Model.

Results are given in table 6.

Table 6

Resins	tau(Pa) at 0.02 D(s ⁻¹)
EB 450	188.2
Example 7	27.63

It can be concluded that the radiation curable modified hyperbranched polyester increase the flow of the ink, resulting in a very low yield value, and improve the appearance.

CLAIMS

1. Modified hyperbranched polyester polyol derived from a hyperbranched polyester polyol comprising a central initiator molecule or initiator polymer having two or more hydroxyl groups, which groups under formation of an initial tree structure are bonded to carboxyl groups of a monomeric chain extender holding hydroxyl groups and carboxyl groups,
5 which tree structure optionally is extended and further branched from the initiator molecule or initiator polymer by an addition of further molecules of a monomeric chain extender by means of bonding between the hydroxyl groups and the carboxyl groups thereof, wherein the hyperbranched polyester polyol is modified via an esterification
10 reaction on at least one hydroxyl group by at least one carboxylic acid and via an acrylation reaction on at least one hydroxyl group by at least another acid chosen among acrylic acid, methacrylic acid and oligomers thereof.
2. Modified hyperbranched polyester polyol according to claim 1, wherein the carboxylic acid
15 is a monocarboxylic acid having at least a molecular weight of 60.
3. Modified hyperbranched polyester polyol according to either preceding claim, wherein the carboxylic acid is lauric acid.
- 20 4. Modified hyperbranched polyester polyol according to any preceding claim, wherein the percentage of free hydroxyl groups is comprises 0 to about 99 % based on initial hydroxyl content of the hyperbranched polyester polyol.
- 25 5. Process for the preparation of a modified hyperbranched polyester polyol according to any preceding claim, characterized in that it comprises a first esterification step in which a hyperbranched polyester polyol is reacted with a carboxylic acid and a second acrylation step in which the compound obtained in the first step is reacted with acrylic acid, methacrylic acid or oligomers thereof.
- 30 6. Process for the preparation of a modified hyperbranched polyester polyol according to any of claims 1 to 4, characterized in that it comprises a first acrylation step in which a hyperbranched polyester polyol is reacted with acrylic acid, methacrylic acid or oligomers thereof, and a second esterification step in which the compound obtained in the first step is reacted with a carboxylic acid.
- 35 7. Process for the preparation of a modified hyperbranched polyester polyol according to any of claims 1 to 4, characterized in that the polyester polyol is reacted with a carboxylic acid

and with acrylic acid, methacrylic acid or oligomers thereof in one step.

8. Process according to claim 5, 6 or 7, wherein the carboxylic acid is a monocarboxylic acid having at least a molecular weight of 60.
- 5
9. Process according to claim 8, wherein the carboxylic acid is lauric acid.
10. Use of a hyperbranched polyester polyol according to claim 1 as component in applications such as binders for radiation curing systems, such as systems cured with ultra-violet (UV) and infra-red (IR) or electron-beam (EB).
- 10
11. Use of a modified hyperbranched polyester polyol according to claim 1 as a resin in a radiation curable ink by addition of pigments and additives.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number
WO 00/77070 A3

- (51) International Patent Classification⁷: C08G 63/91, 63/60, 83/00, C09D 11/10 (74) Agent: KIRK, Martin; UCB, S.A., Intellectual Property Dept., Allée de la Recherche 60, B-1070 Bruxelles (BE).
- (21) International Application Number: PCT/EP00/05191 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 6 June 2000 (06.06.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/138,285 9 June 1999 (09.06.1999) US (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): UCB, S.A. [BE/BE]; Allée de la Recherche 60, B-1070 Bruxelles (BE).
- Published:
— with international search report
- (72) Inventors; and
(75) Inventors/Applicants (*for US only*): VERSCHUEREN, Kris [BE/BE]; E. De Blutslaan 38, B-1702 Groot-Bijgaarden (BE). VANOVERVELT, Jean-Claude [BE/BE]; Rue Albert 26, B-7548 Warchin (BE). DE MICHELI, Philippe [BE/BE]; Rue de Marchienne 146, B-6110 Montigny-Le-Tilleul (BE). (88) Date of publication of the international search report: 2 August 2001
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 00/77070 A3

(54) Title: MODIFIED HYPERBRANCHED POLYESTER POLYMERS, PROCESSES FOR PREPARING THEM AND USES OF THEM

(57) Abstract: Hyperbranched polyester polyols are modified by esterification with a carboxylic acid and the introduction of acrylate or methacrylate groups. By this consecutive or mixed end-capping the modified hyperbranched polyester polyols can be tailored to obtain either very specific or mixed properties. It is possible to use these modified hyperbranched polyester polyols in new industrial applications, such as inks.

Best Available Copy

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/05191

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G63/91 C08G63/60 C08G83/00 C09D11/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 17060 A (PERSTORP AB) 2 September 1993 (1993-09-02) cited in the application	1-5,8-10
Y	claims 1-9; figure 1; examples 1,24,39,47 page 6, paragraph 6 -page 8, paragraph 3 ---	11
Y	DATABASE WPI Section Ch, Week 198932 Derwent Publications Ltd., London, GB; Class A14, AN 1989-232374 XP002160049 & JP 01 168767 A (TOYO INK MFG CO), 4 July 1989 (1989-07-04) abstract --- -/--	11



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

12 February 2001

Date of mailing of the international search report

21/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Krische, D

INTERNATIONAL SEARCH REPORT

Int'l .onal Application No

PCT/EP 00/05191

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JOHANSSON, M. ET AL: "SYNTHESIS, CHARACTERIZATION, AND UV CURING OF ACRYLATE FUNCTIONAL HYPERBRANCHED POLYESTER RESINS" JCT. JOURNAL OF COATINGS TECHNOLOGY, PHILADELPHIA, PA, US, vol. 67, no. 849, October 1995 (1995-10), pages 35-39, XP000925849 ISSN: 0361-8773 page 35 -page 36</p> <p>-----</p>	<p>1,2,4,6, 8,10</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/05191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9317060 A	02-09-1993	SE 468771 B AT 165609 T AU 3653093 A CA 2117486 A,C DE 69318295 D DE 69318295 T DK 630389 T EP 0630389 A ES 2115762 T HK 1005487 A JP 2574201 B JP 7504219 T KR 158912 B SE 9200564 A US 5418301 A	15-03-1993 15-05-1998 13-09-1993 02-09-1993 04-06-1998 01-10-1998 07-10-1998 28-12-1994 01-07-1998 08-01-1999 22-01-1997 11-05-1995 15-01-1999 15-03-1993 23-05-1995
JP 1168767 A	04-07-1989	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.